Un 32t

Technical Paper 336

DEPARTMENT OF THE INTERIOR
HUBERT WORK, SECRETARY
BUREAU OF MINES
H. FOSTER BAIN, DIRECTOR

OXIDATION OF ZINC VAPOR BY CARBON DIOXIDE

BY
B. M. O'HARRA

THE LIBRARY OF THE
DEC 16 1924
UNIVERSITY OF ILLINOIS

THIS PAPER REPRESENTS WORK DONE UNDER A COOPERATIVE AGREEMENT BETWEEN THE BUREAU OF MINES, DEPARTMENT OF THE INTERIOR, AND THE MISSOURI SCHOOL OF MINES AND METALLURGY

WASHINGTON
GOVERNMENT PRINTING OFFICE
1924

Generated on 2024-09-29 22:46 GMT / https://hdl.handle.net/2027/uiug.30112111813504
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from
UNIVERSITY OF ILLINOIS AT
URBANA-CHAMPAIGN

The Bureau of Mines, in carrying out one of the provisions of its organic act—to disseminate information concerning investigations made—has printed a limited free edition of this publication.

When this edition is exhausted, copies may be purchased at cost from the Superintendent of Documents, Government Printing Office, Washington, D. C.

The Superintendent of Documents *is not an official of the Bureau of Mines.* His is an entirely separate office and he should be addressed:

SUPERINTENDENT OF DOCUMENTS,
Government Printing Office,
Washington, D. C.

The general law under which publications are distributed prohibits the giving of more than one copy of a publication to one person. The price of this publication is 5 cents.

First edition, September, 1924.

Generated on 2024-09-29 22:43 GMT / https://hdl.handle.net/2027/uiug.30112111813504
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

CONTENTS

	Page
Introduction	1
Causes of blue-powder formation	2
Physical blue powder	2
Chemical blue powder	3
Conditions giving rise to carbon dioxide in the gases resulting from the reduction of zinc ores	3
Acknowledgments	6
Investigation of the reaction $Zn+CO_2 \rightleftharpoons ZnO+CO$	6
Apparatus used	6
Experiments on the reduction of zinc oxide by mixtures of carbon dioxide and carbon monoxide	8
First experiments	8
Gas mixture containing 6.3 carbon dioxide	9
Gas mixtures containing 19 and 23 per cent carbon dioxide	9
Gas mixture containing 71 per cent carbon dioxide	9
Gas mixture containing 90 per cent carbon dioxide	10
Conclusions	10
Preliminary experiments on the oxidation of zinc vapor by mixtures of carbon dioxide and carbon monoxide	11
Log of an experiment	11
Explanation of results	13
Summary of information from preliminary experiments with zinc	13
Final experiments on the oxidation of zinc vapor	14
Log of an experiment	15
Results of the final experiments	15
Discussion of the experimental results	17
Comparison with Fulton's equilibrium curve	18
Oxidation of zinc vapor by carbon monoxide	19
Summary	21

ILLUSTRATIONS

	Page.
FIGURE 1. Equilibria of the reaction $CO_2+C \rightleftharpoons 2CO$	4
2. Apparatus used for investigating the reaction $Zn+CO_2 \rightleftharpoons ZnO+CO$	7
3. Reaction tube at the end of experiment 24	12
4. Reaction tubes from two typical experiments of the final series	16
5. Percentage of CO_2 required to oxidize zinc in a mixture of CO_2+CO saturated with zinc vapor	17
6. Superposed curves showing concentrations of CO_2 in equilibrium with zinc and with carbon	19

Generated on 2024-09-29 22:41 GMT / https://hdl.handle.net/2027/uiug.30112111813504
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

OXIDATION OF ZINC VAPOR BY CARBON DIOXIDE

By B. M. O'Harra

INTRODUCTION

The problem of the efficient condensation of zinc vapor to liquid zinc, though it has always been of great importance in zinc metallurgy, has not been satisfactorily solved. Ordinarily a large proportion of the volatilized zinc does not condense to liquid, but is obtained as the fine dust called blue powder. Only with difficulty and by taking special precautions can this powder be caused to melt and to coalesce into liquid, consequently a second distillation and condensation usually is necessary to obtain the zinc in liquid form.

In an ordinary retort smelting plant 20 to 25 per cent of the retorts are required continuously for the redistillation of blue powder, and from 25 to 35 per cent of the total zinc produced is obtained from these retorts. In other words, in the primary distillation of zinc from its ores, about one-third of the zinc vapor condenses as blue powder, and only about two-thirds as liquid zinc.

All attempts at smelting zinc ores in a blast furnace have failed, because the zinc has always been obtained as a mixture of zinc oxide and blue powder.

Most of the electrothermic processes that have been tried have also encountered this difficulty, and but few of them have succeeded in obtaining high yields of liquid zinc from the primary distillation. The electric zinc-smelting works in Scandinavia, which are the only ones at present using an electrothermic process on a commercial scale, have abandoned the effort to obtain liquid zinc from the first smelting operation. Formerly they redistilled the blue powder produced from the primary distillation of the ore, but in recent years have found that the powder can be melted by heating it to a temperature above the melting point and subjecting it to rubbing action.[1-2]

American metallurgists who have experimented with electrothermic processes have progressed somewhat further and a few have

[1-2] Ingalls, W. R., Electrometallurgy of zinc: Trans. Am. Electrochem. Soc., vol. 40, 1921, pp. 245–257. Cornelius, C. E., Electric rotating furnace for melting zinc powder, U. S. patent 1396677, November 8, 1921; British patent 170026, April 13, 1920. Huldt, Sven, Method of converting zinc powder into liquid zinc: U. S. patent 1266808, May 21, 1918; Condenser for zinc vapors, U. S. patent 1311604, July 29, 1919. Berglund, E. S., Extracting zinc in electric furnaces, British patent 120549, 1918.

Generated on 2024-09-29 22:44 GMT / https://hdl.handle.net/2027/uiug.30112111813504
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

succeeded in obtaining satisfactory yields of liquid zinc in one operation. W. McA. Johnson reports one furnace run in which 77.87 per cent of the total zinc condensed was liquid.[3] C. H. Fulton has said that no blue powder was formed during his experiments on a semi-commercial scale at East St. Louis in 1916 and 1917.[4]

In spite of these exceptions, preventing the formation of blue powder is still a troublesome problem in all pyrometallurgical processes for treating zinc ores, and a complete knowledge concerning the various causes of blue-powder formation would be of much value to zinc metallurgists.

CAUSES OF BLUE-POWDER FORMATION [5]

A detailed enumeration of all the causes of blue-powder formation includes so many physical and chemical factors that it is difficult to correlate them properly or to determine their relative importance, but the more important of them are quite generally recognized. They may be classified as physical causes and chemical causes, for the two act quite differently; the blue powder produced by physical causes and that produced by chemical causes have decidedly different characteristics.

PHYSICAL BLUE POWDER

The production of physical blue powder is largely regulated by the design and temperature control of the condenser. When zinc vapor is condensed, that which condenses at temperatures above 419° C. is obtained in the molten condition, either in drops or as a liquid body; that which condenses below 419° C. forms solid crystals similar to snow or frost. From a mixture of equal parts by volume of zinc and carbon monoxide, such as is produced in the reduction of zinc oxide by carbon, only a fraction of 1 per cent of the zinc remains uncondensed at 419° C., so that it is theoretically possible to obtain nearly all of the zinc as liquid.

Most of the condensation normally takes place at the inner surface of the condenser walls, which, because they are continually radiating heat outward, are cooler than the vapor coming in contact with them. The zinc condenses upon this surface as liquid drops which increase in size until they coalesce and run to the bottom of

[3] Johnson, W. McA., The commercial aspect of electric zinc-lead smelting: Trans. Canadian Min. Inst., vol. 17, 1914, pp. 107–129.

[4] Fulton, C. H., Electric resistance furnace of large capacity for zinc ores: Trans. Am. Inst. Min. and Met. Eng., vol. 64, 1920, pp. 188–226.

[5] O'Harra, B. M., The electrothermic metallurgy of zinc: Bull. 208, Bureau of Mines, 1923, pp. 78–85; see also Richards, J. W., Metallurgical calculations, 1918, pp. 643–653; Stansfield, Alfred, The electric furnace, 2 ed., 1914, pp. 325–332; and the review of Lemarchands, Contribution a l'étude de la métallurgie du zinc: Rev. métall., t. 17, Dec., 1920, pp. 803–841.

Generated on 2024-09-29 22:41 GMT / https://hdl.handle.net/2027/uiug.30112111813504
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

the condenser to form a liquid bath. However, the zinc vapor must diffuse through the diluting carbon monoxide to come in contact with the condenser walls. This diffusion requires an appreciable time, and hence if the vapor is cooled too suddenly, or the distance through which the vapor must diffuse in order to reach the condenser walls is too great, the zinc will condense in the gas stream as minute droplets that will be carried along to the cooler region of the condenser and will solidify before they can coalesce. By cooling the vapor from a zinc retort very rapidly in a condenser that has a large ratio of volume to surface all the zinc can be condensed as this "physical blue powder."

True physical blue powder is nearly pure zinc and contains very little zinc oxide or other impurities. Its production is analogous to the production of flowers of sulphur, a chilled condenser being necessary. If heated under pressure in a reducing atmosphere, physical blue powder can be melted to liquid zinc.

CHEMICAL BLUE POWDER

Chemical blue powder is caused by the formation of a solid film on the surface of newly formed minute globules of liquid zinc as condensation progresses. The film prevents the globules from coalescing to larger liquid masses, even though the temperature conditions may be correct. This film may consist of zinc oxide, zinc sulphide, or similar zinc compounds caused by such gases as carbon dioxide, water vapor, or sulphur compounds formed in the retort, or by air diffused through the walls of the retort and condenser; or it may consist simply of fine dust carried over from the retort. Chemical blue powder usually contains considerable amounts of zinc oxide and smaller amounts of other impurities.

Of the detrimental gases that tend to cause the formation of chemical blue powder, carbon dioxide is most important. There are always small amounts of it in the gases that result from the reduction of zinc ores by carbon, and under certain conditions large amounts may be present.

CONDITIONS GIVING RISE TO CARBON DIOXIDE IN THE GASES RESULTING FROM THE REDUCTION OF ZINC ORES

Most metallurgists believe that the reduction of zinc oxide by carbon takes place in two stages:

$$ZnO+CO=Zn+CO_2$$
$$CO_2+C=2CO$$

Both of these reactions are reversible and the direction in which each will proceed at any given temperature and pressure depends upon the relative proportions of zinc vapor, carbon monoxide, and carbon dioxide present.

Generated on 2024-09-29 22:45 GMT / https://hdl.handle.net/2027/uiug.30112111813504
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

The equilibrium conditions of the reaction $CO_2+C \rightleftharpoons 2CO$ have been studied by several investigators,[6] the investigation of Rhead and Wheeler being the most complete and reliable. The curves in Figure 1 show the percentages of carbon dioxide in mixtures of carbon

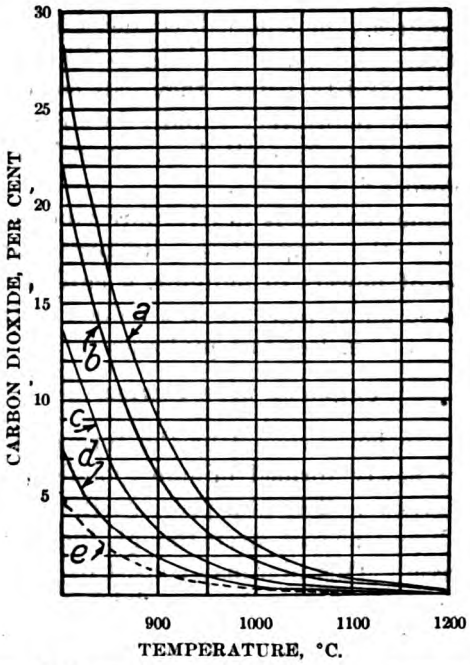

FIGURE 1.—Equilibria of the reaction $CO_2+C \rightleftharpoons 2CO$ at: *a*, 3 atmospheres pressure; *b*, 2 atmospheres pressure; *c*, 1 atmosphere pressure; *d*, ½ atmosphere pressure; *e*, ⅓ atmosphere pressure.

dioxide and carbon monoxide in equilibrium with solid carbon at various temperatures and pressures, as determined by their experiments.

---

[6] Boudouard, O., Sur la décomposition de l'oxyde de carbone en présence de l'oxyde de fer: Compt. rend., t. 128, 1899, pp. 98–101; Sur lo décomposition de l'oxyde de carbone en présence des oxydes métalliques: Compt. rend., t. 128, 1899, pp. 822–24; Sur la décomposition de l'acide carbonique en présence du charbon: Compt. rend., t. 128, 1899, pp. 824–25; Sur la décomposition de l'oxyde de carbone en présence des oxydes métalliques: Compt. rend., t. 128, 1899, pp. 1522–23; Sur la décomposition de l'acide carbonique en présence du charbon: Compt. rend., t. 128, 1899, pp. 1524–25; Recherches sur les equilibres chimiques: Ann. chim. et phys., t. 24, 1901, pp. 5–85.

Schenck, R., and Zimmerman, F., Über die Spaltung des Kohlenoxyds und das Hochofengleichgewicht: Ber. Deut. chem. Gesell., Jahrg. 36, 1903, pp. 1231–1251.

Schenck, R., and Heller, W., Über die gegenseitigen Beziehungen der verschiedenen Kohlenstoffmodificationen: Ber. Deut. chem. Gesell., Jahrg. 38, 1905, pp. 2139–2143.

Rhead, T. F. E., and Wheeler, R. V., The effect of temperature on the equilibrium $2CO \rightleftharpoons CO_2+C$: Jour. Chem. Soc., vol. 97, 1910, pp. 2178–2189; The effect of temperature and pressure on the equilibrium $2CO \rightleftharpoons CO_2+C$: Jour. Chem. Soc., vol. 99, 1911, pp. 1140–1153; The rate of reduction of carbon dioxide by carbon: Jour. Chem. Soc., vol. 101, 1912, pp. 831–845.

Lewis, G. N., and Randall, Merle, The free energy of some carbon compounds: Jour. Am. Chem. Soc., vol. 37, 1915, pp. 458–470.

Generated on 2024-09-29 22:47 GMT / https://hdl.handle.net/2027/uiug.30112111813504
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

The curves indicate that at the temperature and pressure of zinc reduction in commercial practice—1,000° to 1,250° C. and 1 atmosphere pressure—carbon dioxide can exist in the presence of solid carbon only in proportions less than 1 per cent, but that at temperatures below 1,000° C. the possible proportion increases until at 800° C. about 14 per cent corresponds to the equilibrium condition.

When the temperature of a charge of zinc oxide containing an excess of carbon is raised slowly and uniformly until the zinc begins to distill, the carbon dioxide formed at the lower temperatures is largely expelled or reduced to carbon monoxide, as the temperature increases, before any zinc vapor is produced, and thereafter not more than a fraction of 1 per cent of carbon dioxide can be formed in the presence of the excess carbon. If, however, the charge is heated unevenly, so that part of it is hot enough to produce zinc vapor while other parts are cold enough for large amounts of carbon dioxide to be formed, the carbon dioxide and zinc vapor will enter the condenser together; the carbon dioxide will tend to oxidize the zinc and a large proportion of blue powder will be formed.

Some source of oxygen is of course required for this formation of carbon dioxide in the cooler parts of the charge. This source may be easily reducible oxides, such as those of lead and iron. Carbon dioxide may also be produced from carbonates introduced into the charge in uncalcined calamine ores.

Heating is especially liable to be uneven in electric furnaces that heat the charge by means of an arc or by the resistance of only a part of the charge, and is most detrimental in those processes in which the residue is melted to a liquid slag, because in those processes it is difficult to provide for an excess of carbon or sufficient contact of the gases with carbon.

Because of the influence of carbon dioxide on zinc condensation, quantitative information as to the amount of carbon dioxide necessary to oxidize zinc vapor in a mixture of zinc vapor, carbon monoxide, and carbon dioxide at various temperatures is of much practical value.

To obtain this information the investigation described in the present paper was undertaken by the Bureau of Mines, in cooperation with the Missouri School of Mines and Metallurgy, at the suggestion of C. H. Fulton, director of that school and consulting metallurgist of the Bureau of Mines. Doctor Fulton[7] had already done some work on the equilibrium of the reaction $Zn+CO_2 \rightleftharpoons ZnO+CO$, and the present investigation is to a certain extent a continuation of that work.

[7] Fulton, C. H., The condensation of zinc from its vapor: Trans. Am. Inst. Min. and Met. Eng., vol. 60, 1919, pp. 280–302.

Generated on 2024-09-29 22:42 GMT / https://hdl.handle.net/2027/uiug.30112111813504
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

The object of the investigation was to determine accurately the ratio of carbon dioxide to carbon monoxide required to oxidize zinc under conditions approaching as nearly as possible those in the ordinary zinc condenser.

ACKNOWLEDGMENTS

The work described in this paper was carried out at the suggestion and under the direction of Doctor Fulton, and to his suggestions and advice is largely due the surmounting of the difficulties that were encountered in finding a suitable method of experiment for obtaining the information desired. The author acknowledges the able assistance of C. W. Burkhart in performing the experimental work. O. C. Ralston, L. E. Roberts, and C. M. Bouton of the Pacific experiment station of the Bureau of Mines helped with the physicochemical phases of the work.

INVESTIGATION OF THE REACTION $Zn+CO_2 \rightleftharpoons ZnO+CO$

APPARATUS USED

Figure 2 is a diagram of the apparatus used in the investigation.

The method first tried for preparing carbon monoxide was to pass carbon dioxide over charcoal heated to 1,100° C. in an electric furnace. The gas prepared by this method contained much hydrogen, which was evidently liberated by the charcoal. Most of the hydrogen came off in the first few liters of gas, but even after prolonged heating the carbon monoxide obtained contained several per cent of it. When coke was used instead of charcoal, the gas was contaminated with impurities such as compounds of sulphur. Granular graphite produced satisfactorily pure gas, but the temperature required for rapid conversion of the carbon dioxide to carbon monoxide was so high that the consumption of combustion tubes was excessive.

The method finally adopted was to warm concentrated sulphuric acid with formic acid, in the flask *c*. The carbon monoxide was freed of carbon dioxide and oxygen by passage through concentrated potassium hydroxide and potassium pyrogallate solutions in washing bottles *d* and *e*. Carbon dioxide was prepared in the Kipp generator *f* from c. p. dilute hydrochloric acid and crystalline marble, and was passed through sodium carbonate solution in the washing bottle *g* to absorb any acid spray or vapor that it might have contained.

The purified carbon monoxide and dioxide flowed into the large gas-storage bottle *b*. The pressure in this storage bottle was regulated by raising or lowering the pressure bottle *a*, which was placed on a small elevator, the storage bottle and pressure bottle being connected by a flexible siphon. When the desired proportions of the

Generated on 2024-09-29 22:44 GMT / https://hdl.handle.net/2027/uiug.30112111813504
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

two gases had been delivered to the storage bottle the gas generators were disconnected from it and the carbon monoxide and carbon dioxide were thoroughly mixed by shaking the storage bottle vigorously. This mixture was purified further by passage over stick phosphorus *h* and through sodium carbonate solution and distilled water in the bottles *i* and *j*, and was then thoroughly dried by pass-

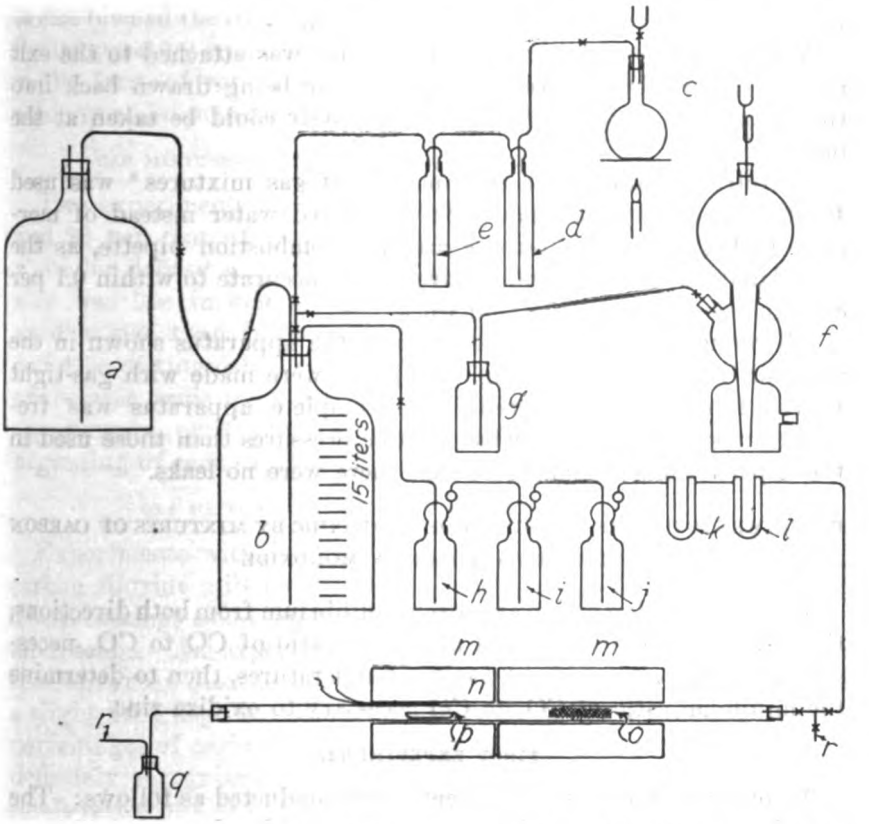

FIGURE 2.—Apparatus used for investigating the reaction $Zn + CO_2 \rightleftharpoons ZnO + CO$: *a*, Pressure bottle; *b*, gas storage-bottle; *c*, CO generator; *d*, KOH solution; *e*, pyrogallic solution; *f*, CO_2 generator; *g* and *i*, Na_2CO_3 solution; *h*, phosphorus; *j* and *q*, distilled water; *k*, anhydrous $CaCl_2$; *l*, P_2O_5; *m*, nichrome-wound electric furnace; *n*, thermocouple; *o*, copper turnings; *p*, zinc in boat; *r*, gas outlets.

ing through the U-tubes *k* and *l*, which contained anhydrous calcium chloride and phosphorus pentoxide, respectively. Finally, the last trace of oxygen was removed by passing the gas over hot copper turnings at *o*.

The zinc or zinc oxide on which the effect of the gas mixture was to be determined was contained in the porcelain or alundum boat *p* heated to constant temperature in the nichrome-wound electric resistance furnace *m*. The temperature of the zinc was read by means

Generated on 2024-09-29 22:41 GMT / https://hdl.handle.net/2027/uiug.30112111813504
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

of a thermocouple *n*, whose junction was placed outside but against the wall of the combustion tube. Comparison of the readings of a thermocouple in this position with the readings of one placed inside the tube showed a difference of less than 5° C. The combustion tube containing the copper turnings and the zinc or zinc oxide was of pyrex glass for all experiments run at temperatures below 750° C. In the few experiments at higher temperatures, combustion tubes of transparent fused quartz were used.

A wash bottle containing distilled water was attached to the exit end of the combustion tube to prevent air being drawn back into the apparatus. Samples of gas for analysis could be taken at the outlets *rr*.

Burrell's apparatus for the analysis of gas mixtures[8] was used for the analysis of the gas, with acidulated water instead of mercury in the measuring burette and the combustion pipette, as the acidulated water was found to give results accurate to within 0.1 per cent and permitted more rapid work.

All connections between the parts of the apparatus shown in the diagram were of glass tubing, and joints were made with gas-tight rubber tubing tightly wired. The complete apparatus was frequently tested under somewhat greater pressures than those used in the experiments, to make sure that there were no leaks.

EXPERIMENTS ON THE REDUCTION OF ZINC OXIDE BY MIXTURES OF CARBON DIOXIDE AND CARBON MONOXIDE

The original plan was to approach equilibrium from both directions, that is, first to determine the minimum ratio of CO to CO_2 necessary to reduce zinc oxide at various temperatures, then to determine the minimum ratio of CO_2 to CO necessary to oxidize zinc.

FIRST EXPERIMENTS

Accordingly the first experiments were conducted as follows: The porcelain boat *p* was filled with c. p. zinc oxide, the apparatus was filled with the carbon monoxide and carbon dioxide mixture of known composition, and the zinc oxide was heated to the desired temperature and held, within a variation of 10° C., at that temperature for an hour. During this time the mixture of carbon monoxide and carbon dioxide was slowly passed through the apparatus. At the end of the hour the upper half of the furnace, which was hinged to the lower half, was raised and the reaction tube was allowed to cool rapidly; the passage of the gas was maintained during cooling. The cold tube was then broken and examined for evidences of the reduction of the zinc oxide.

[8] Burrell, G. A., and Seibert, F. M., The sampling and examination of mine gases and natural gas: Bull. 42, Bureau of Mines, 1913, p. 43 (Fig. 17).

Generated on 2024-09-29 22:45 GMT / https://hdl.handle.net/2027/uiug.30112111813504
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

GAS MIXTURE CONTAINING 6.3 PER CENT CARBON DIOXIDE

In the first of these experiments with zinc oxide, the gas mixture contained 6.3 per cent carbon dioxide. The temperature was held at 755° C. At the end of the experiment a thick coating of zinc was found in the cooler part of the tube near the end of the furnace, most of it as bright metallic globules which gradually diminished in size toward the cold end of the tube. In the part of the tube where the temperature was below the melting point of zinc, the deposit was in the form of very fine frosty crystals. A slight coating of zinc oxide was also present with the metallic zinc.

GAS MIXTURES CONTAINING 19 AND 23 PER CENT CARBON DIOXIDE

Two experiments using gas mixtures that contained 19 per cent and 23 per cent of carbon dioxide at the same temperature gave a similar deposit of zinc plus a small amount of zinc oxide, but the zinc was less in amount and was deposited in globules of much smaller size than in the first experiment. The separate globules could be distinguished only with a microscope. The loss in weight of the zinc oxide in the boat was 0.0150 and 0.0151 gram for the two experiments, or 3 per cent of the one-half gram present at the beginning of each experiment.

GAS MIXTURE CONTAINING 71 PER CENT CARBON DIOXIDE

Experiments with gas mixtures containing higher percentages of carbon dioxide still gave metallic coatings mixed with zinc oxide. These coatings could not be resolved into separate globules under the microscope. An experiment with a gas mixture containing 71 per cent of carbon dioxide and 29 per cent of carbon monoxide gave only a slight dark deposit. The coatings obtained in the presence of high percentages of carbon dioxide were so scanty that they could not be definitely recognized as zinc. Reduction of zinc oxide with such small ratios of CO to CO_2 had not been expected and it was at first thought that these dark deposits might be either carbon, formed by the reaction $2CO \rightleftharpoons CO_2 + C$, or some easily reducible impurity from the zinc oxide. The coatings were, however, soluble in dilute hydrochloric acid, so could not have been carbon; and when tested by heating in air, they were oxidized to a white oxide, yellow when hot, which would indicate that they were really zinc.

Although this very slight reduction in the presence of such large percentages of carbon dioxide was unexpected, upon second thought it can be explained readily. The equilibrium condition of the reaction $ZnO + CO \rightleftharpoons Zn + CO_2$ is expressed by

$$\frac{\text{Conc. ZnO} \times \text{conc. CO}}{\text{Conc. Zn} \times \text{conc. CO}_2} = K$$

where K is a constant for any given temperature and pressure. In the experiments just described, where zinc oxide was present in the

Generated on 2024-09-29 22:42 GMT / https://hdl.handle.net/2027/uiug.30112111813504
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

solid phase, the concentration of ZnO was constant, but as there was no liquid zinc present in the zone of reaction at 750° C., the concentration of zinc vapor was a variable and the equilibrium condition may be expressed by

$$\frac{\text{Conc. CO}}{\text{Conc. Zn} \times \text{conc. CO}_2} = K'$$

From this it may be seen that as the concentration of CO_2 was increased the concentration of zinc vapor which could be present must have decreased, but that even with very high concentrations of CO_2 slight traces of zinc vapor could exist. Consequently even with these high percentages of carbon dioxide a slight reduction of the zinc oxide was to be expected.

GAS MIXTURE CONTAINING 90 PER CENT CARBON DIOXIDE

In one experiment similar to the preceding ones but with 90 per cent of carbon dioxide in the gas mixture, no metallic or dark coating was obtained in the reaction tube, but there was a noticeable deposit of zinc oxide in the part of the tube where the zinc had been found in the previous experiments, and the zinc oxide in the boat showed a loss in weight of 0.001 gram, or 0.2 per cent. To determine whether this deposit of zinc oxide and that found associated with the metallic zinc in the other experiments were due to actual volatilization of zinc oxide, a test was run under the same conditions except that air was used instead of the mixture of carbon monoxide and carbon dioxide. In this test but a barely perceptible trace of zinc oxide was deposited on the walls of the tube, hence the transfer of zinc oxide before noted must have been due to reduction of zinc at the reaction temperature of 750° C., followed by a reoxidation in the cooler portions of the tube.

This result would indicate that in the reaction $ZnO+CO \rightleftharpoons Zn+CO_2$ equilibrium requires a decreasing concentration of CO_2 and an increasing concentration of CO with decreasing temperature, and corroborates the experiments of Lencauchez.[9]

CONCLUSIONS

Although the experiments with zinc oxide were interesting, it became evident that no quantitative information could be expected from them since there was no way of determining the concentration of zinc vapor present, and the ratio of carbon monoxide to carbon dioxide necessary for equilibrium depended on this variable.

It was then decided to approach equilibrium from the opposite direction; that is, to determine the minimum ratio of carbon dioxide to carbon monoxide necessary to oxidize zinc. By starting with

[9] Lencauchez, A., Métallurgie du zinc; de la condensation des vapeurs de zinc dans les appareils soufflés: Mem. Soc. ing. civ., 1877, pp. 568–580.

Generated on 2024-09-29 22:42 GMT / https://hdl.handle.net/2027/uiug.30112111813504
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

metallic zinc instead of zinc oxide there would always be an excess of liquid zinc in the reaction zone, so that if the gas mixture were not passed over the zinc too rapidly the concentration of zinc vapor would be constant at any given temperature, corresponding to the vapor pressure of zinc at that temperature.[10]

PRELIMINARY EXPERIMENTS ON THE OXIDATION OF ZINC VAPOR BY MIXTURES OF CARBON DIOXIDE AND CARBON MONOXIDE

Procedure in the experiments with zinc was the same as in those with zinc oxide. The sample of zinc,[11] weighing 10 to 20 grams, was placed in the boat *p* (see Fig. 2), the apparatus was filled with the carbon monoxide-carbon dioxide mixture, and the zinc was heated to the desired temperature and held constant at that temperature for an hour, the passage of the gas mixture being continued during that time and during the subsequent cooling of the reaction tube. At the end of the hour the top half of the furnace was raised and the tube cooled rapidly. The appearance of the deposit was noted, and the deposit was examined visually both from the outside and, after the tube was broken, from the inside for signs of oxidation.

The approximate total volume of gas passed during the hour and the weight of zinc lost from the boat were noted. To make sure that this volume of gas was actually saturated with zinc vapor the weight of zinc volatilized was compared with that theoretically required for saturation at the temperature of the experiment. When the velocity of the gas stream was moderate (up to 2 liters an hour) there was always more zinc volatilized than was required for saturation. This excess was undoubtedly due to two things: (1) Distillation of zinc from a region of high vapor pressure to one of low vapor pressure, and (2) convection currents in the reaction tube, whereby gas saturated with zinc vapor in the hot part of the tube would be carried to the cooler part, deposit part of its zinc, and be returned to the hotter part to become again saturated at the higher temperature.

LOG OF AN EXPERIMENT

Below is the log of a typical one of these preliminary experiments (experiment 24, January 16, 1922).

Started to heat furnace at 9.30 a. m. Gas leaving reaction tube contained 0.8 per cent CO_2.

---

[10] For data on the vapor pressure of zinc, see Barus, Carl, High-temperature work in igneous fusion and ebullition, chiefly in relation to pressure: U. S. Geol. Survey Bull. 103, 1893, 57 pp.; Phil. Mag., vol. 29, 1890, p. 141. Johnston, John, The vapor pressure and volatility of several high-boiling metals; a review: Jour. Ind. and Eng. Chem., vol. 9, Sept., 1917, pp. 873–878.

[11] The zinc used was stick zinc furnished by the New Jersey Zinc Co. and had about the following analysis: Pb, .0004 per cent; Fe, .005 per cent; Cd, .0018 per cent; As, trace; S, trace; Sb, not found; Sn, not found; Zn, 99.993 per cent.

Generated on 2024-09-29 22:48 GMT / https://hdl.handle.net/2027/uiug.30112111813504
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

Temperature reached 753° C. at 9.50 a. m. and was held at that point until 10.50 a. m.

Analysis of gas leaving reaction tube at 9.50 a. m.

	Per cent
Carbon dioxide (CO_2)	0.6
Oxygen (O_2)	None.
Carbon monoxide (CO)	95.2
Hydrogen (H_2)	[a] 0.4
Nitrogen (N_2)	3.8

[a] The gas leaving the reaction tube in all these experiments contained 0.1 per cent to 0.5 per cent hydrogen and 0.5 per cent to 3.0 per cent nitrogen. The hydrogen probably was derived from traces of water vapor, which remained in the tube even after very thorough drying and was reduced to hydrogen by the reaction $H_2O + CO = H_2 + CO_2$. The nitrogen was introduced into the system by being dissolved in the water in the pressure bottle *a* (Fig. 2), and later liberated in the storage bottle *b* as the water flowed from *a* to *b*.

Samples taken at 10.15 and 10.45 a. m. of the gas leaving the reaction tube contained no CO_2 whatever, though another sample of the gas entering the tube at 10.45 still contained 0.8 per cent CO_2.

A total of 1.65 liters of gas was passed during the hour 9.50 to 10.50 a. m.

	Grams
Weight of zinc in boat at beginning of experiment	21.3365
Weight of zinc in boat at finish of experiment	19.8902
Weight of zinc volatilized	1.4463

There is required 0.64 gram of zinc to saturate 1.65 liters of gas at 750° C. The excess is explained by distillation and convection currents as described above.

Figure 3 shows the appearance of the reaction tube at the end of the experiment.

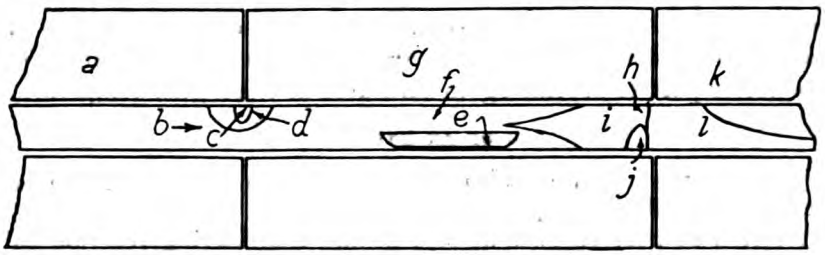

FIGURE 3.—Reaction tube at the end of experiment 24: *a*, Furnace for heating copper turnings; *b*, direction of gas flow; *c*, zinc; *d*, faint coating of ZnO; *e*, zinc in boat; *f*, temperature 750° C.; *g*, heating furnace; *h*, temperature about 450° C.; *i*, bright zinc globules; *j*, ZnO coating; *k*, cold section of furnace; *l*, physical blue powder (bright frosty crystals).

The zinc in that region of the tube which had a temperature of 750° C. showed no sign of oxidization with this gas, which contained 0.8 per cent CO_2, and as the zinc vapor passed into the cooler parts

Generated on 2024-09-29 22:41 GMT / https://hdl.handle.net/2027/uiug.30112111813504
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

of the tube it was deposited as bright unoxidized globules until it reached a part of the tube where the temperature was about 450° C. Here a coating of ZnO formed. Beyond that part of the tube the zinc, though deposited as crystalline blue powder because of the temperature at which it condensed being below its melting point, was again bright and unoxidized. The gas leaving the reaction tube contained no CO_2.

EXPLANATION OF RESULTS

A reasonable explanation of these facts is that a mixture of carbon monoxide and carbon dioxide containing 0.8 per cent of carbon dioxide has no oxidizing effect on zinc at 750° C. or at somewhat lower temperatures, but at about 450° C. and below the mixture does have an oxidizing effect, and as the temperature falls all the carbon dioxide in the gas reacts with the zinc to form zinc oxide. The small amount of carbon dioxide in the original gas that entered the reaction tube in this experiment was quickly used up, leaving an excess of zinc which was deposited farther along the tube as bright unoxidized crystals. Thus this experiment also indicated that equilibrium requires a decreasing concentration of carbon dioxide as temperature decreases.

Similar experiments with slightly higher percentages of CO_2 gave similar results except that oxidation started at somewhat higher temperatures. An experiment with a gas mixture containing 10 per cent of carbon dioxide resulted in a deposit of zinc which was heavily oxidized throughout. It was found that, no matter what percentage of carbon dioxide was in the gas entering the reaction tube, if the gas current was slow enough to allow time for the reaction to go to completion the gas leaving the tube would contain no carbon dioxide, this having been completely used in forming zinc oxide.

SUMMARY OF INFORMATION FROM PRELIMINARY EXPERIMENTS WITH ZINC

Although these preliminary experiments with zinc gave additional interesting information on the oxidation of zinc by carbon dioxide and the change of the equilibrium conditions of the reaction with varying temperature, they supplied little more quantitative information than did the experiments with zinc oxide. The composition of the gas leaving the reaction tube did not represent the proportions of carbon dioxide and carbon monoxide at equilibrium with zinc and zinc oxide at the temperature of the experiment, but at some indefinite lower temperature. Again, the mere fact that the zinc deposit showed oxidation in any given experiment did not prove that the mixture of carbon dioxide and carbon monoxide had had an

Generated on 2024-09-29 22:45 GMT / https://hdl.handle.net/2027/uiug.30112111813504
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

oxidizing effect at the temperature concerning which information was desired, since the oxidation might have taken place at lower temperature in a cooler part of the tube.

Measurement of the temperature of the hottest part of the reaction tube at which zinc oxide was formed when a given percentage of carbon dioxide was used might have given the desired information, but as the temperature fell from that of the heating furnace to that of the room within a relatively short length of the tube, the temperature at any particular point within this range of variation could not be determined accurately.

It was decided that a series of experiments similar to those just described, but with certain conditions controlled more closely, and with the observations interpreted in the light of what had been learned in the preliminary experiments, would give rather definite information as to the percentage of carbon dioxide required to oxidize zinc at various temperatures under conditions much like those existing in the zinc condenser as used in metallurgical practice. This series of experiments gave consistent results and is described on the following pages.

FINAL EXPERIMENTS ON THE OXIDATION OF ZINC VAPOR

In these final experiments the procedure was the same as in the preceding ones. The rate of flow of the gas mixture through the reaction tube was controlled more closely and so regulated that as nearly as possible 2 liters of gas were passed during the time of the experiment, which was one hour as before. This volume of gas contained sufficient carbon dioxide so that, if there were any oxidation of the zinc enough zinc oxide would be formed to be plainly visible, and yet the rate of flow was slow enough to allow complete saturation of the gas with zinc vapor.

At the end of the experiment the reaction tube, cooled rapidly while still filled with the gas mixture, was examined for evidence of oxidation *in the part of the tube in which the boat containing the zinc had been, and the temperature of which corresponded to that indicated by the pyrometer.* If oxidation had taken place in that part of the tube the mixture of carbon dioxide and carbon monoxide used in the experiment was known to be oxidizing to zinc at that particular temperature; if no oxidation had taken place there the mixture was known to be reducing, or at least nonoxidizing. Oxidation in the cooler parts of the tube was ignored as it was caused by reaction at a lower temperature.

Generated on 2024-09-29 22:42 GMT / https://hdl.handle.net/2027/uiug.30112111813504
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

LOG OF AN EXPERIMENT

The log of a representative experiment of this final series (Experiment 41, February 23, 1922) follows:

Started to heat furnace at 2 p. m.

Analysis of gas leaving reaction tube at 2 p. m.

	Per cent
Carbon dioxide (CO_2)	5.3
Oxygen (O_2)	None.
Carbon monoxide (CO)	91.0
Hydrogen (H_2)	0.8
Nitrogen (N_2)	2.9

Temperature reached 715° C. at 2.15 p. m. and was held there until 3.15 p. m.

The gas entering the reaction tube at 3.15 contained 6 per cent CO_2.

Two liters of gas were passed during the hour 2.15 to 3.15 p. m.

	Grams
Weight of zinc plus boat at beginning of experiment	21.1065
Weight of zinc plus boat at finish of experiment	20.7365
Weight of zinc volatilized	0.3700

The weight volatilized is approximately equal to the theoretical weight of zinc required to saturate 2 liters of gas at 715° C.

Examination of the reaction tube at the end of the experiment showed no oxidation in that region of the tube where the temperature had been held at 715° C. A mixture of carbon dioxide and carbon monoxide containing 5.7 per cent carbon dioxide therefore has no oxidizing effect on zinc at this temperature when the mixture is saturated with zinc vapor.

RESULTS OF THE FINAL EXPERIMENTS

Figure 4 illustrates the appearance of two reaction tubes from typical experiments at the same temperature but with different proportions of carbon dioxide. Of these, *A* is a tube showing no oxidation at the temperature of the experiment, although showing oxidation at lower temperature and *B* is a tube showing oxidation at the temperature of the experiment. A small amount of zinc oxide will be noted at the cool part of both tubes where the stream of gas entered the reaction zone and encountered the slight amount of zinc that diffused backward against the direction of flow of the gas. The oxidation that occurred at this point was not enough to change the proportion of CO_2 appreciably in the gas reaching the reaction zone.

Generated on 2024-09-29 22:46 GMT / https://hdl.handle.net/2027/uiug.30112111813504
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

A series of experiments as just described was run at five different temperatures, 50° C. apart, from 615° to 815° C., with varying percentages of carbon dioxide at each temperature. The results were plotted on cross-section paper, with the percentages of carbon dioxide in the gas as abscissas and the temperatures in degrees centigrade as ordinates. A smooth curve was then drawn as a boundary line as nearly as possible between the region of the plot which showed oxidation and that which showed no oxidation. This curve, with the

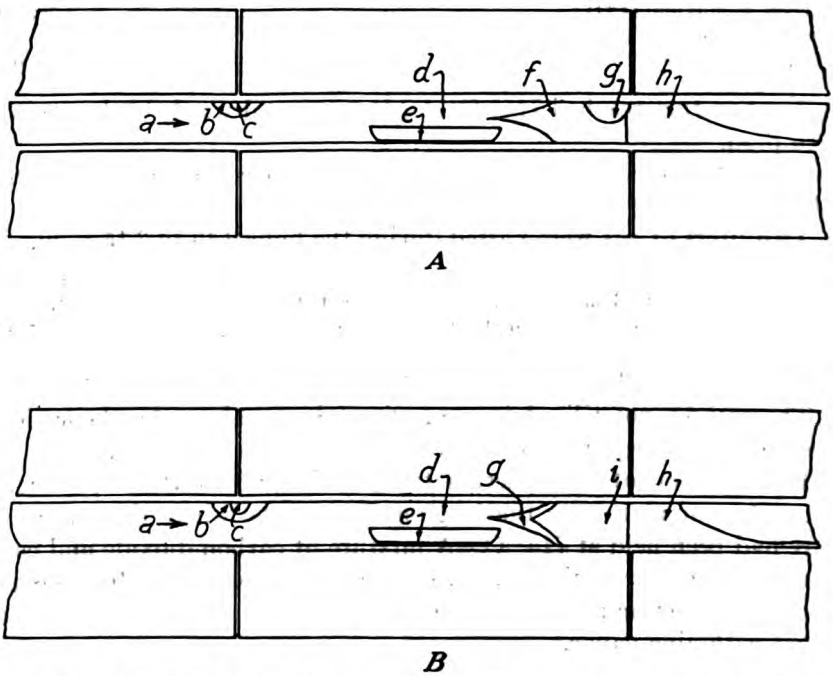

FIGURE 4.—Reaction tubes from two typical experiments of the final series: *A*, No oxidation at 715° C.; *B*, oxidation at 715° C.: *a*, Direction of gas flow; *b*, faint coating of ZnO; *c*, zinc; *d*, temperature 715° C.; *e*, zinc in boat; *f*, bright zinc globules; *g*, ZnO coating; *h*, physical blue powder; *i*, zinc globules with some ZnO.

result of each individual one of the final experiments, is shown in Figure 5. As will be seen, these results with but two or three exceptions are consistent and the boundary between the regions of oxidation and nonoxidation is quite well defined.

In using this curve one must remember that the curve is directly applicable only to mixtures of carbon dioxide, carbon monoxide, and zinc vapor *that are saturated with zinc vapor*. If less than this proportion of zinc vapor is present, larger concentrations of carbon dioxide are required to cause oxidation. In the metallurgical condensation of zinc vapor the gases are, of course, saturated with zinc

Generated on 2024-09-29 22:43 GMT / https://hdl.handle.net/2027/uiug.30112111813504
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

vapor at all temperatures below that at which condensation starts (about 860° C.).

DISCUSSION OF THE EXPERIMENTAL RESULTS

The investigation that has been described was undertaken, as explained before, to obtain information concerning the effect of carbon dioxide upon the condensation of zinc vapor from the gases evolved during the commercial reduction of zinc ores. The original plan was to determine the true equilibrium conditions at various temperatures of the reversible reaction

$$Zn + CO_2 \rightleftharpoons ZnO + CO.$$

Determination of the equilibrium conditions of similar reactions involving nonvolatile metals is readily accomplished by several

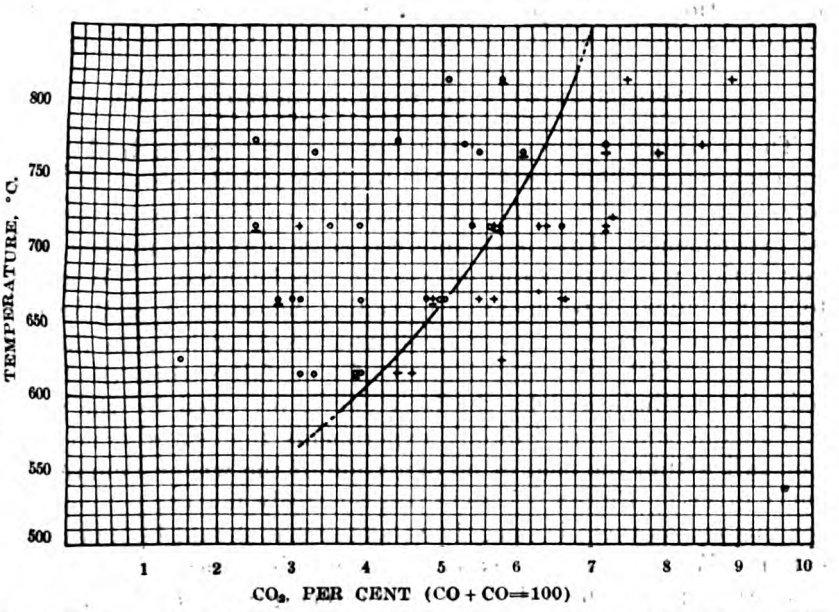

FIGURE 5.—Percentage of CO_2 required to oxidize zinc in a mixture of $CO_2 + CO$ saturated with zinc vapor. Symbols: o, No oxidation; +, oxidation; o and ±, doubtful.

methods. The volatility of zinc, however, introduces difficulties that prevent the use of the more usual methods. The method finally used for these experiments duplicates very closely the conditions of zinc condensation in actual practice and hence furnishes data that are of especial interest to the practical zinc metallurgist. It may give approximately the equilibrium conditions of the reaction, but as equilibrium was approached from one direction only, it is perhaps doubtful whether the curve shown in Figure 5 gives accurately the true equilibrium conditions. An investigation of the true equilibrium

Generated on 2024-09-29 22:42 GMT / https://hdl.handle.net/2027/uiug.30112111813504
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

conditions of the reaction is now being made at the Pacific experiment station of the Bureau of Mines at Berkeley, Calif.

An attempt was made to determine by means of thermodynamic calculations how closely the values given by the experimental curve approach true equilibrium values. On the assumption that the curve was accurate at 800° C., the equilibrium concentration of carbon dioxide shown by the curve at this temperature was used in calculating the equilibrium concentration of carbon dioxide at 600° C. This calculated value indicated that the equilibrium curve should slope more to the left with decreasing temperature than does the experimental curve. The calculation, however, involved the use of specific heat data of doubtful accuracy, so that for the present the question must remain unsettled. The problem is largely of academic interest, since the curve given certainly indicates with fair accuracy the situation that the practical zinc metallurgist must face, regardless of whether or not it represents true equilibrium conditions.

COMPARISON WITH FULTON'S EQUILIBRIUM CURVE

The equilibrium curve for this same reaction given by Fulton in his earlier paper [12] slopes from left to right with decreasing temperature, or in an opposite direction to that derived from the present series of experiments. This is of interest, since Fulton's method of investigation was similar to that used in this later work. When Fulton's individual experiments are studied, however, it will be noted that the proportions of carbon dioxide used by him in those experiments which showed oxidation of zinc fall within the field of oxidation as indicated by the later curve, prepared by the writer; and in the same way Fulton's experiments that showed no oxidation fall within the field of no oxidation of the writer's curve. The curve given by Fulton is based upon relatively few experiments, and for this reason there is some doubt as to what should be its exact location. With these few experiments it might seem reasonable to draw the curve as he did, since he obtained greater oxidation at the higher temperatures than at the lower ones in experiments with the same concentration of CO_2. This result now seems to have been due to the greater rate of reaction at the higher temperatures, and not to a decrease in the proportion of carbon dioxide necessary for equilibrium.

The number and position of the points derived from the present series of experiments, as plotted in Figure 5, define the position of the boundary curve much more definitely and permit for it no position greatly differing from that given. The slope of this curve is

[12] Fulton, C. H., The condensation of zinc from its vapor: Trans. Am. Inst. Min. and Met. Eng., vol. 60, 1919, pp. 280–302.

Generated on 2024-09-29 22:41 GMT / https://hdl.handle.net/2027/uiug.30112111813504
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

further corroborated by the preliminary experiments with zinc oxide and by the observations made during the preliminary experiments with zinc. Furthermore, theoretical considerations demand that the true equilibrium curve must slope from right to left with decreasing temperature. The reaction $Zn+CO_2 \rightleftharpoons ZnO+CO$, taking place from left to right, is exothermic, and therefore according to the law of Le Chatelier and Braun requires for equilibrium an increasing concentration of CO_2 with increasing temperature.

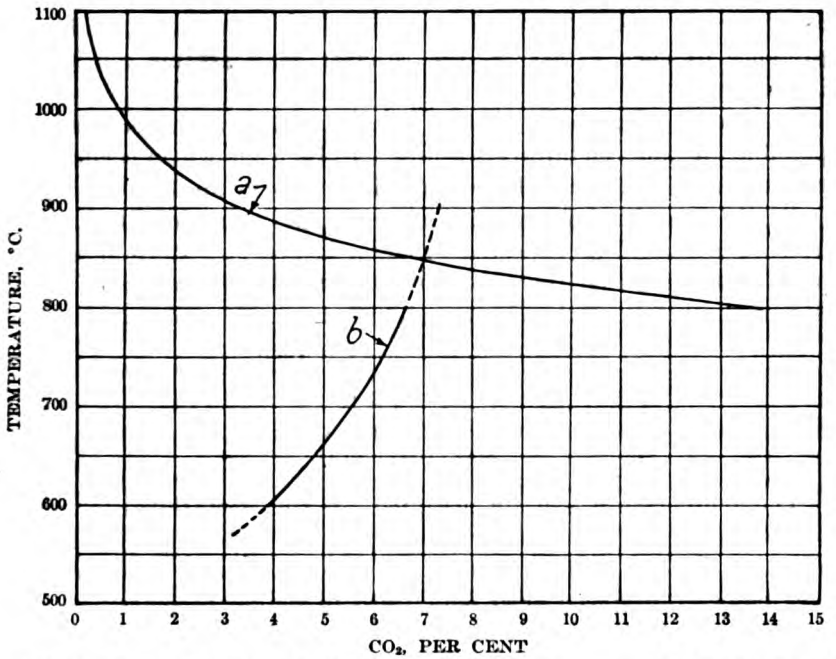

FIGURE 6.—Superposed curves showing: *a*, Equilibrium of the reaction $CO \rightleftharpoons CO_2 + C$ at 1 atmosphere pressure; *b*, equilibrium of the reaction $Zn + CO_2 \rightleftharpoons ZnO + CO$ at 1 atmosphere pressure.

OXIDATION OF ZINC VAPOR BY CARBON MONOXIDE

In Figure 6 the curve of Rhead and Wheeler for the equilibrium of the reaction $2CO \rightleftharpoons CO_2 + C$ at 1 atmosphere pressure and the curve showing that of the reaction $Zn+CO_2 \rightleftharpoons ZnO+CO$ are plotted together. The figure brings out clearly an interesting relation. The two curves intersect at 850° C. and at lower temperatures the concentration of carbon dioxide in equilibrium with solid carbon is greater than the concentration that can exist in equilibrium with zinc; hence, in a mixture of zinc vapor and carbon monoxide, the decomposition of carbon monoxide into carbon and carbon dioxide can produce enough of the latter to cause oxidation of the zinc vapor,

Generated on 2024-09-29 22:42 GMT / https://hdl.handle.net/2027/uiug.30112111813504
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

and the net result is oxidation of the zinc by carbon monoxide as represented by the equations:

$$2CO=CO_2+C$$
$$\underline{Zn+CO_2=ZnO+CO}$$
$$Zn+CO=ZnO+C$$

The practical importance of this series of reactions is limited by the exceedingly low velocity of the reaction $2CO=CO_2+C$ under ordinary conditions. Certain substances, notably metallic iron, act as catalyzers in greatly increasing the rate of this reaction, and in the presence of such catalyzers the reaction may assume considerable importance.

Oxidation of zinc by carbon monoxide has been recognized as possible by zinc metallurgists and has been shown experimentally by Lemarchands,[13] though he found it to be very slight.

By the same line of reasoning as above, the reduction of zinc oxide by carbon should be expected to begin at 850° C., since at all temperatures above that the concentration of carbon monoxide in equilibrium with solid carbon is enough to reduce zinc oxide and the reactions should take place in the following sequence:

$$CO_2+C=2CO$$
$$\underline{ZnO+CO=Zn+CO_2}$$
$$ZnO+C=Zn+CO$$

The temperature usually accepted by zinc metallurgists for the beginning of the reduction of zinc oxide by carbon is between 950° and 1,050° C. This temperature, however, is that at which a visible zinc flame is produced or at which loss in weight becomes noticeable in a comparatively short time, and is probably higher than the temperature at which slight reduction first starts. Bodenstein and Schubart, by a series of very careful experiments in which they measured the maximum pressure of zinc vapor plus carbon monoxide developed by the reaction at different temperatures, found that the reduction of zinc oxide by carbon was possible at a minimum temperature of 780° C. at atmospheric pressure, but that the reduction was exceedingly slow at these low temperatures.[14]

P. Pierron, by thermochemical calculations, placed the minimum temperature at which reduction is possible under atmospheric pressure at 826° C.[15]

---

[13] Lemarchands, M., Contribution a l'étude de la métallurgie: Rev. métall., t. 17, Dec., 1920, pp. 803–841.

[14] Bodenstein, M., Die physikalisch-chemischen Grundlagen der hüttenmännischen Zinkgewinnung: Ztschr. Elektrochem., Jahrg. 23, 1917, pp. 105–116.

[15] Pierron, P., Sur la condensation des vapeurs de zinc: Ann. de l'energie, Jan., 1922.

Generated on 2024-09-29 22:43 GMT / https://hdl.handle.net/2027/uiug.30112111813504
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

These three values—850°, 780°, and 826° C.—agree fairly well considering the difficult nature of the determinations and the uncertain accuracy of the data upon which the thermal calculations are based.

Bodenstein and Schubart found that the velocity of reduction was much slower when the zinc oxide had previously been heated to a high temperature. This probably explains why those who have determined the temperature at which reduction first becomes visibly noticeable have found that this temperature is higher when the zinc oxide has been heated to a high temperature previously and that it varies with the physical form of the carbon used. It does not seem plausible that the true equilibrium temperature, above which reduction first becomes possible, should vary with the physical characteristics of the reacting substances, except where a change from one allotropic form to another constitutes a true change of the solid phase.

SUMMARY

Because of the important effect of carbon dioxide on the condensation of zinc vapor in the metallurgical treatment of zinc ores, experiments were made to determine the concentration of carbon dioxide necessary to oxidize zinc vapor at various temperatures.

Although the preliminary experiments failed to give the quantitative information desired, they proved that the required concentration of carbon dioxide increased with rising temperature. It was found that zinc oxide was reduced at 750° C.[16] by carbon monoxide even when carbon dioxide was present in large proportions, but that partial reoxidation took place in the cooler part of the reaction tube. The weight of zinc oxide reduced in a given time decreased with increasing ratios of carbon dioxide, and when 90 per cent of carbon dioxide was present the reduction and reoxidation was manifest only by a transfer of zinc oxide from the hot to the cooler part of the tube.

In the preliminary experiments with zinc it was found that oxidation took place in the cooler parts of the reaction tube, even when the concentration of carbon dioxide was not enough to oxidize zinc in the hot part of the tube. It was furthermore found that all carbon dioxide was converted to carbon monoxide by reaction with zinc at some temperature between 750° C. and room temperature, if enough time were allowed for the completion of the reaction.

With the knowledge gained from these preliminary experiments a final series of experiments was planned, from which the desired quantitative data were obtained. These data were plotted and a

[16] The experiments on the reduction of zinc oxide were carried on only at 750° C. Lemarchands found that reduction took place at temperatures as low as 300° to 350° C.

Generated on 2024-09-29 22:45 GMT / https://hdl.handle.net/2027/uiug.30112111813504
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

curve drawn from which may be found the minimum concentration of carbon dioxide at any given temperature that will have an oxidizing effect on zinc vapor under the conditions of zinc condensation in metallurgical practice.

It has also been demonstrated that the oxidation of zinc vapor by carbon monoxide is theoretically possible, though this oxidation is ordinarily of little practical importance.

Generated on 2024-09-29 22:46 GMT / https://hdl.handle.net/2027/uiug.30112111813504
Public Domain, Google-digitized / http://www.hathitrust.org/access_use#pd-google
Digitized by Google
Original from UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN